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(56) Documents cited

GB 1499759

GB 1423341

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GB 1340859

GB 1174770

GB 1113795

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(54) Treatment of textiles

(57) A method of treating textiles comprises applying to the textile a water-soluble curable polymeric material in an aqueous medium, simultaneously or subsequently applying to the textile a compatible exhaustion agent which reduces the solubility of the polymeric material, allowing the polymeric material to exhaust onto the textile and curing the polymeric material.

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## SPECIFICATION

## Treatment of textiles

- 5 This invention relates to the treatment of textiles, in particular with water soluble polymeric materials. 5

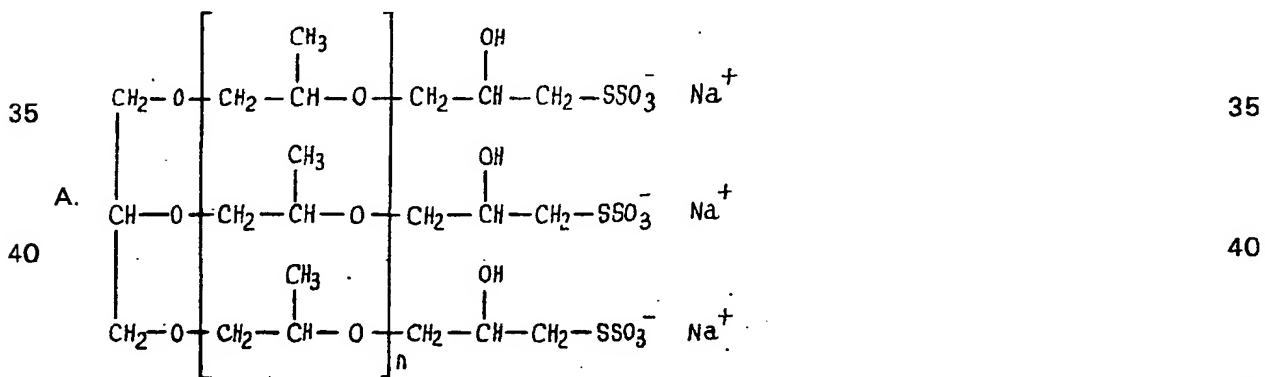
Polymeric materials such as the Bunte salt compounds disclosed in our British Patent No. 1,423,342 or the poly(carbamoylsulphonates) disclosed in British Patent No. 1,419,306 are especially suitable as textile finishing agents, in particular in conferring shrink resistance on keratinous textile materials such as wool. 10

Such resins have hitherto been applied to textile piece goods principally by means of pad mangles. Pad mangles are relatively expensive and not at all textile finishers have one. Accordingly, the invention seeks to provide a process of finishing textiles, from either short or long liquors, which may be carried out in widely available wet processing equipment following a simple processing route and using only inexpensive auxiliary chemicals. 15

According to the present invention there is provided a method of treating textiles which comprises applying a water-soluble curable polymeric material, optionally in the presence of alkali, in an aqueous medium to the textile, simultaneously or subsequently applying a compatible exhaustion agent, allowing the polymeric material to exhaust onto the textile, and curing the polymeric material. The term 'curing' includes allowing to cure. 20

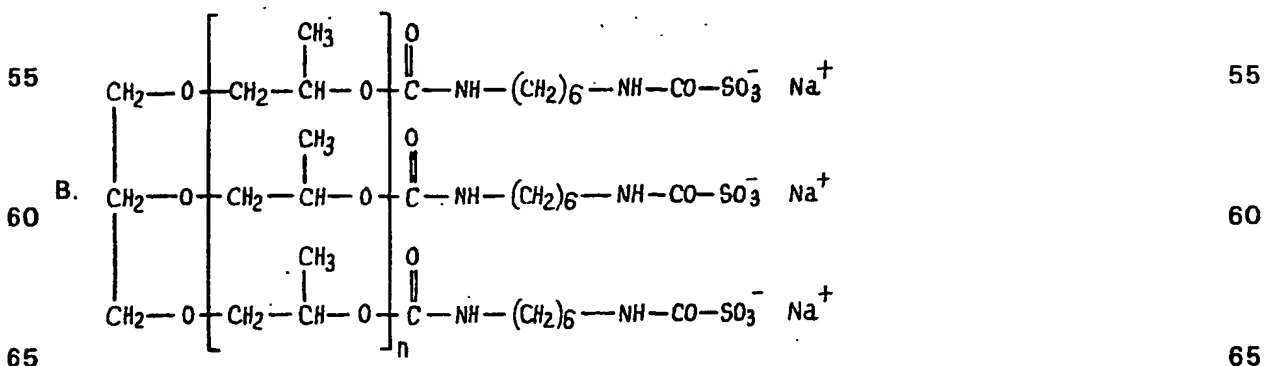
The process is generally applicable to water-soluble curable polymers and especially those having ionic charges. Examples of suitable polymers include polycarbamoyl sulphonates, Bunte salt polymers, the amphoteric polymers of our British Patent Application No. 9467/75, anionic acrylate emulsions, cationic polymers such as polyamide-epichlorhydrin polymer, azetidinium polymers, and blocked polyisocyanate emulsions (made ionic by addition of an anionic surfactant). 25

Preferred curable polymeric materials have a polymeric chain backbone and at least two thiosulphate groups per molecule. The chain may advantageously be a polyoxyalkylene, e.g. polyoxypropylene, chain. Particularly preferred materials of this type have the following structural formula: 30



where n is about 13.

Other polymeric materials useful in the process of the invention include poly(carbamoylsulphonates). These may conveniently be prepared from polymeric di- or poly-isocyanates by treatment with sodium bisulphite. Preferred poly(carbamoylsulphonates) have polyoxyalkylene, e.g. polypropylene, backbones and three carbamoylsulphonate groups. Particularly preferred poly(carbamoylsulphonate) have the following formula: 50



where n is about 13.

In general, the amount of polymeric material applied will be between  $\frac{1}{2}$  and 10% on the weight of the fibres (o.w.f.), with amounts in the range of 2 to 4% o.w.f. being preferred.

- 5 Curing routes for the polymer include: removing the goods from the treatment bath after exhaustion and curing at high temperature (e.g. 120 to 160°C), preferably in a stenter; or removing the goods after exhaustion, drying them at, say, 50°C, and then steaming them to effect curing. 5

- Alkalis promote cross-linking or curing of the polymeric material. It is frequently advantageous to pre-mix an alkali with the polymeric material for an ageing period to provide a partially cross-linked, or activated, polymer before application to the textile. This is particularly advantageous when operating at short liquor ratios. Typically ageing periods of 10 to 60 minutes may be employed. At long liquor ratios it may be advantageous to raise the pH of the liquor by addition of alkali at or towards the end of the exhaustion to promote curing although this is not essential and curing by other methods such as heat curing is possible. Any alkali may be used, for example 10 linked, or activated, polymer before application to the textile. This is particularly advantageous when operating at short liquor ratios. Typically ageing periods of 10 to 60 minutes may be employed. At long liquor ratios it may be advantageous to raise the pH of the liquor by addition of alkali at or towards the end of the exhaustion to promote curing although this is not essential and curing by other methods such as heat curing is possible. Any alkali may be used, for example 15 alkali metal carbonates or hydroxides, but particularly good results are obtained using ammonium hydroxide or, at short liquor ratios, trisodium phosphate. 15

- When an alkali is used the amount of alkali present is advantageously sufficient to ensure an alkaline reaction of the treatment liquor, preferably a pH value of 8 to 10. In a long liquor it is desirable to ensure that the weight of alkaline compound present or added is sufficient to achieve an alkaline reaction on the textile, which may contain residual acid from a previous process, for example carbonization. 20

- The exhaustion agent may be any soluble compound which reduces the solubility of the polymeric material and does not react adversely with the other compounds present and is preferably ionic in character, especially an inorganic salt. In general, any neutral metal salt may be used. Particularly useful are alkali metal, alkaline earth or ammonium salts of strong acids, 25 e.g.  $\text{Na}_2\text{SO}_4$ , NaI, NaCl,  $\text{MgSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$  and especially  $\text{MgCl}_2$ . It appears that salts of divalent metals are twice as effective, on a weight basis, as salts of monovalent metals. The amounts required vary with the nature of the compound, but in general between 1 and 100 g/l preferably 5 to 10 g/l may be used. Trivalent or polyvalent salts, e.g.  $\text{AlCl}_3$  or  $\text{FeCl}_3$ , may 30 be used but, since they act very quickly, care must be taken to ensure level treatments. 30

The process of the invention can be applied using long or short liquors. When using short liquors, typically 1:1 to 3:1, the liquor is virtually completely absorbed by the textile goods. The preferred processing sequence is as follows:

- (i) the polymeric compound and an alkali are mixed and allowed to age; 35  
(ii) the liquor from (i) is applied to the goods in a washing machine or milling machine;  
(iii) the goods are agitated until a uniform distribution of the liquor is obtained;  
(iv) a solution of inorganic salt is sprayed onto the goods and agitation continued until it is evenly distributed; and  
(v) the goods are rinsed, hydroextracted and dried. 40

- 40 In order to avoid any risk of slight discoloration of the goods being treated it is preferred to add a mild bleaching at a late stage in the process. Suitable agents include oxidising agents such as hydrogen peroxide, and reducing agents such as bisulphites.

- No separate curing step is needed since the polymer is fully cured at the end of step (iv). Furthermore, the process can be carried out at room temperature and so energy costs are kept 45 to a minimum. 45

- In order to check that the liquor is evenly distributed at the end of steps (iii) and (iv) sighting colours may be used. For example, a pink sighting colour added to the initial liquor will colour the goods a level pink colour when step (iii) is completed. If a blue sighting colour is added with the salt solution the end of step (iv) can be ascertained when the goods are an even purple 50 colour. Both sighting colours will wash out completely during the rinsing step. 50

- The short liquor ratio process can be carried out in any short liquor processing apparatus capable of agitating the goods, preferably with a tumbling action. Washing machines are especially suitable. For knitwear, e.g. Shetland sweaters, which is generally subjected to a milling operation, the process may be carried out in the milling machine.

- 55 When the process is applied using long liquors, typically at liquor ratios from 10:1 up to, say, 100:1, and especially in the range 20:1 to 30:1, suitable machinery includes side-paddle machines, winch machines, beam machines and dolly washers. The preferred processing sequence for long liquor ratios is as follows: 55

- (i) the polymer is added to the bath containing the goods set at a pH between 5 and 8;  
(ii) a solution of the inorganic salt is added and the temperature raised to 50°C; 60  
(iii) after exhaustion is complete (usually in 30 to 60 minutes) alkali is added to pH 9–10; and  
(iv) after a further 15 to 30 minutes the goods are hydroextracted and dried;

- This sequence involving steps (iii) and (iv) allows the goods to be dyed in the same bath 65 without intermediate drying, thus saving a processing step. 65

Thus it can be seen that both long and short liquor processes may be carried out simply using common and inexpensive chemicals in widely available apparatus using a short and simple treatment cycle.

While the process may be used in finishing textiles generally it is especially applicable to 5 textiles of keratinous fibres such as wool. With the latter, resistance to area felting shrinkage during subsequent laundering is conferred. 5

The process is applicable to textiles in forms varying from loose stock, sliver, top and yarn to piece goods and garments. It has been found particularly useful with knitted piece goods and garments, especially Shetland or lambswool knitwear.

10 When long liquors are employed, it will be observed that, as the temperature approaches 50°C, the polymer/salt solution becomes milky in appearance, whereas if the temperature is increased it goes clear again. Best results are obtained when carrying out the process at or near the temperature of maximum turbidity. 10

It is preferred that the goods should be free from dirt, grease or spinning oils and therefore 15 pre-scouring in a detergent solution, preferably non-ionic, is recommended. Similarly a non-ionic or anionic detergent may be added to the liquor to ensure complete wetting-out of the goods during processing. 15

The following Examples are given to illustrate the invention. The preparation or origin of the polymeric compounds employed in Examples 8 to 60 are as follows.

20 *Preparation of Amphoteric Polymers* 20

Two polymers were prepared in accordance with the disclosures of our British Applications Nos. 9467/75 and 28569/77, one using the H<sub>2</sub>SO<sub>4</sub> route and a second using the toluene sulphonic acid route. These are designated APS 1 and APS II respectively.

25 *Preparation of APS 1* 25

67.5 g of synthappret LKF (an 80% solids isocyanate-terminated prepolymer—Bayer A.G.) were dissolved in 25 g of dry ethyl acetate. 1.57 g H<sub>2</sub>SO<sub>4</sub> (A.R. 100%) was added and the reaction mixture stirred for 45 minutes. 50 g isopropyl alcohol, 12.5 g dioxan and 4.5 g of 30 sodium metabisulphite dissolved in 15 cm<sup>3</sup> water were then added. The reaction mixture was brought to pH 5 with the addition of 0.5 g sodium dicarbonate. The reaction was followed spectrophotometrically. The product was acidified with 5 g HCl (conc.). Analysis of the product showed it to contain 57% cationic groups and 43% anionic groups. 30

35 *Preparation of APS II* 35

150 g of Synthappret LKF were dissolved in a 16 g dioxan–4 g ethylacetate mixture. 8 g of dried toluene sulphonic acid monohydrate was added with stirring, reaction being complete in 25 minutes. 150 g isopropyl alcohol and 9 g of sodium metabisulphite, dissolved in 70 cm<sup>3</sup> water, were added to the reaction mixture. The reaction mixture was brought to pH 5 with 3 g 40 sodium bicarbonate and stirred continuously. The reaction was followed spectrophotometrically. On completion the product was acidified with 15 g HCl. Analysis showed the product to contain 55% cationic groups and 45% anionic groups. 40

#### *Preparation of Acetone Oxime Blocked Polyisocyanate*

45 300 parts by weight (0.1 mole) of a 3000 molecular weight polypropylene oxide triol were dried by heating under vacuum for 30 minutes at 120°C. After cooling and blanketing the polyol with nitrogen, 57.4 parts by weight (0.33 mole) of 2,4-toluene diisocyanate were added and the temperature of the reaction mixture was maintained at 75°C until analysis of the reaction mixture showed that 45.5% of the isocyanate groups originally present had reacted. 50 The polyisocyanate was then cooled to 35°C and 26.3 parts by weight (0.36 moles) of acetone oxime were added and the mixture stirred to dissolve the acetone oxime. Stirring was continued until infra-red analysis indicated that all the isocyanate groups present had reacted with the acetone oxime. 50

The adduct was diluted to an 80% solution by the addition of 106 parts by weight of toluene.

55 An aqueous emulsion of this product was prepared by dissolving 10 parts by weight of Atlab Test Surfactant HLB 10 (Honeywill Atlas) in 100 parts by weight of the solution of the blocked polyisocyanate. This solution was transferred to a high shear mixer and 210 parts by weight of water were added whilst mixing with high shear to form a 25% solids emulsion of the blocked polyisocyanate. 60

#### *Other Polymeric Preparations*

"Impranil DLH" is an anionic aliphatic polyester urethane dispersion free from organic solvents and emulsifiers, supplied by Bayer AG as a 40% aqueous dispersion. "Impranil DLN" and "Impranil 4693" are of similar constitution.

65 Polyacrylate E 1070 is a self cross-linking polyacrylate emulsion supplied by Rohm and Haas 65

(UK) Ltd. as a 46% aqueous emulsion.

Hercosett 57 is a polyamide-epichlorohydrin resin supplied by Hercules.

The bisulphite addition product (BAP) of Synthappret LKF was prepared by known techniques, as described in British Patent No.

5 The amount of polymer applied is indicated in % on the weight of wool (oww). 5

#### Wash Test

In the Examples, fabric samples were wash tested in a 'Cubex' washing machine in 15 litres of pH 7 phosphate buffer solution at 40°C with a 1 kg load including, where necessary, 10 makeweights. Area felting shrinkage results are given as percentage change in area after 1 hour or 3 hours washing. 10

#### Example 1

Unscoured Shetland wool swatches (2/8's worsted count yarn; knitted to cover factor 0.85) 15 (1 kg) were prescoured in a Wascator washing machine using a solution containing a non-ionic detergent (Lissapol NX, ICI) 2 g/l, sodium sulphate 2 g/l and sodium metabisulphite 2% o.w.f. Scouring was carried out at 40°C for 10 min.; the goods were then rinsed well and hydroextracted to 50% pick-up. 15

An activated emulsion of Bunte salt polyether polymer was prepared by dissolving trisodium 20 phosphate (30.0 g) in 1,920 ml of water and then adding 80 ml of a Bunte salt polyether (Lankrolan SHR<sub>3</sub>, Lankro Chemicals Ltd.) (40% solids) (i.e. 16 g/l Bunte salt polymer, 15 g/l Na<sub>3</sub>PO<sub>4</sub>). Duratint Pink (5 g/l) was also added at this stage. This solution was allowed to age for 30 minutes before adding to the prescoured wool goods. (Allowing for the water remaining on the goods from prescouring this gives a liquor ratio of 2.5:1). 20

25 The addition of the activated polymer emulsion to the goods in the Wascator machine may be made either by spraying directly onto the goods with the machine switched on to give a tumbling action, or simply by pouring onto the bulk of the material prior to tumbling. In this Example, tumbling was carried out for thirty minutes during which time the pink tinted solution rapidly redistributes itself evenly along the knitted swatches; even those swatches which were 30 quite white at the start of the tumbling cycle were observed to be evenly tinted showing that the liquor had distributed itself evenly. 30

At this point 500 ml of a blue tinted 6% (w/v) solution of sodium chloride was added to the Wascator, again either by spraying or simply by pouring onto the bulk of the swatches. (The effective liquor ratio was then 3:1).

35 Tumbling was carried out for a further 15 min., when it was seen that all the swatches were uniformly pre-tinted. The swatches were then rinsed with cold water to remove both the tints and the inorganic salts. Hydroextraction and drying completed the process. 35

Three sample swatches were taken from the front, centre and back of the machine and without drying were subjected to the 15-litre Cubex wash test. The following results were 40 obtained:- 40

		% Area shrinkage		
45 Sample	1 hour wash	3 hour wash		45
Front of machine	- 2	0		
Centre of machine	1	1		
Back of machine	- 3	- 1		
50 Scoured only	35	61		50

Negative values indicate an extension

#### Example 2

55 The procedure of Example 1 was essentially followed, except that processing was carried out in a "Cherry Tree" milling machine commonly used for milling woollen garments. Again, good machine washability without intermediate drying was obtained. 55

#### Example 3

60 An all wool woven worsted 2/2 twill fabric was scoured in the usual way and then placed in a conventional fabric milling machine. An activated ( $\frac{1}{2}$  hour aged) liquor (16 g/l Lankrolan SHR<sub>3</sub>, 15 g/l trisodium phosphate) was prepared as in Example 1 and 100 kg added slowly by pouring directly onto the moving fabric (40 kg). The pressure on the throat of the milling machine was adjusted so that after 15 minutes 6% width shrinkage had occurred. After this 65 time the pressure was relaxed and after running for a further 15 minutes it was seen that level 65

distribution of the liquor over the fabric had been produced. At this stage 50 kg of a 6% sodium chloride solution was added and the fabric run a further fifteen minutes under very little throat pressure. Rinsing with water, hydroextraction and drying completed the process.

Cubex testing (15 litre, 3 hours) gave zero area shrinkage compared with 43% for the untreated fabric.

#### Example 4

Shetland fabric (2/8's worsted count yarn knitted to cover factor 0.85) was scoured and milled in Lissapol NX (2 g/l) and anhydrous sodium sulphate (2 g/l). The wool was then rinsed. In a fresh bath at 20°C and 30:1 liquor ratio, 1.5 g/l 0.880 ammonia was added followed 5 minutes later by 3.5% (solids) o.w.f. Lankrolan SHR 3. 15 g/l sodium chloride was then added and the whole raised to 50°C over 10 min. Exhaustion to about 90% occurred over 30 min. whereupon a further 5 g/l sodium chloride was added and circulation continued for a further 30 min. At this stage the wool passed the I.W.S. Superwash (TM 185) felting shrinkage test (1st hour 0%; 2nd hour 1%; 3rd hour 2%). However, it was conventionally hydroextracted and tumble dried at 90°C for 15 min., when the shrinkage figures were found to be similar to those of the undried fabric.

#### Example 5

The Shetland fabric of Example 4 was scoured and milled. A stock solution was made up containing 80 g/l Lankrolan SHR3 and 20 g/l ammonia. This was aged for 30 min. The scoured and milled wool was wetted out at a liquor ratio of 30:1 at 20°C and the bath brought to pH 9 by the addition of ammonia. The resin stock was then added to a dosage level of 3.5% o.w.f. resin solids followed by 15 g/l sodium chloride. The bath was raised to 50°C and circulated for 30 min. A further 5 g/l sodium chloride was then added and circulation continued for 30 min.

The goods were then hydroextracted and tumble dried (90°C, 15 min.) and Cubex tested:—

	1 hour	2 hour	3 hour
Area shrinkage: —	1	3	5

If Cubex testing is carried out before drying, equally good results are recorded, indicating that polymer crosslinking occurs on the fabric before drying.

#### Example 6

A worsted serge fabric was treated on a winch machine by the method of Example 2. After hydroextraction and drying, the fabric was Cubex tested and found to give an area shrinkage value (3 hour, 15-litre test) of 0%. The untreated fabric gave a value of 43%.

#### Example 7

Shetland wool samples are scoured and milled as in Example 4.

The procedure of Example 4 was then followed except that 10 g/l magnesium sulphate was added instead of the sodium chloride. The pH of the treatment liquor was 9.5

The temperature was raised to 50°C over 10 min. and then held at 50° for 5 min., whereupon 2% o.w.f. of sodium metabisulphite was added and the bath run a further 15 min. at the same temperature.

The samples were then hydroextracted and the following wash test results obtained on samples which had been air dried or tumble dried.

	Ar a shrinkage %		
	1 hour wash	2 hour wash	3 hour wash
Air dried	1	2	3
Tumble dried	0	0	1

#### Examples 8–10

The fabric was a plain weave unbleached wool flannel fabric of weight 185 g.m<sup>-2</sup>. It was scoured with 1 g/l non-ionic detergent (Lissapol N, ICI) and 2 g/l Na<sub>2</sub>CO<sub>3</sub> at 40°C for 10

minutes, followed by rinsing.

Samples of the fabric were run in a bath of liquor ratio 40:1 set at 50° and pH 7, containing 2.0% (solids) oww BAP and 10 g/l of either of the following metal salts: MgCl<sub>2</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>. The temperature was maintained at 50°C until exhaustion took place. The wool was then either

- (i) rinsed and dried at 140° for 15 minutes (heat cure),
- (ii) dried at 50°C for 15 minutes and steamed 5 minutes (steam cure), or
- (iii) cured in the treatment bath by raising the pH to 9 and holding for 30 minutes followed by drying at 50°C for 15 minutes (bath cure).

Example No	Metal salt	Time to Exhaustion (min.)	Area Shrinkage (%)					
			Heat Cure		Steam Cure		Bath Cure	
			1 hr	3 hr	1 hr	3 hr	1 hr	3 hr
8	MCl <sub>2</sub>	35	3	11.5	2	8	3	5
9	CaCl <sub>2</sub>	20	9.5	25	8	19	4	12
10	ZaSO <sub>4</sub>	180	4	19	3.5	15	4	11
Untreated fabric			1 hr wash 32%, 3 hr 45%					

#### Examples 11-13

Samples of scoured flannel were run in a bath of liquor ratio 40:1 set at pH 7 and 50°C, containing 1% (solids) oww BAP, 1% (solids) Impranil DLH and 10 g/l of one of the following metal salts: MgCl<sub>2</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>.

The temperature was maintained at 50°C until exhaustion took place. The polymers were then cured as in Examples 8-10.

Example	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)					
			Heat Cure		Steam Cure		Bath Cure	
			1 hr	3 hr	1 hr	3 hr	1 hr	3 hr
11	MgCl <sub>2</sub>	25	4.5	18	4	10	1.5	5
12	CaCl <sub>2</sub>	12	10	25	4	13	4	15
13	ZnSO <sub>4</sub>	90	4	175	6	20	7	24

#### Examples 14-19

Samples of flannel were run in a bath of liquor ratio 40:1 set at 50°C and pH 7, containing either 4.0% (solids) oww APS I or 4.0% (solids) oww APS II and 10 g/l of one of the following metal salts; MgCl<sub>2</sub>, CaCl<sub>2</sub>, ZnSO<sub>4</sub>. The temperature was maintained at 50°C until exhaustion took place. Samples were then cured as in Examples 8-10.

50	Example	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)						50
				Heat Cure		Steam Cure		Bath Cure		
				1 hr	3 hr	1 hr	3 hr	1 hr	3 hr	
	APS I									
55	14	MgCl <sub>2</sub>	15	7	27	2	13	1	8	55
	15	CaCl <sub>2</sub>	15	3	24	2	20	3.5	18	
	16	ZnSO <sub>4</sub>	25	2	8	3.5	10	0	1	
	APS II									
60	17	MgCl <sub>2</sub>	30	5	25	0	9	0	7	60
	18	CaCl <sub>2</sub>	30	4	28	0	11	2	10	
	19	ZnSO <sub>4</sub>	45	0	5	1	5	0	0	

#### Examples 20-22

Samples of scoured flannel were run in a bath of liquor ratio 40:1 set at pH 7 and 50°C

containing 4.0% (solids) acetone oxime blocked polyisocyanate, 0.5 g/l sodium lauryl sulphate and 10 g/l of one of the following metal salts:  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{ZnSO}_4$ . The temperature was maintained at 50°C until exhaustion was complete. The polymer was the cured either by:

- (i) heating the sample to 140°C for 15 minutes, or  
 (ii) drying at 50°C for 15 minutes followed by steaming for 5 minutes.

Example No	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)			
			Heat Cure		Steam Cure	
			1 hr	3 hr	1 hr	3 hr
20	$\text{MgCl}_2$	45	0	1	0	1.5
21	$\text{CaCl}_2$	45	2	6	2	2.5
22	$\text{ZnSO}_4$	60	0	1	0	7

#### Examples 23–24

The procedure of Example 8 was repeated using 5% (solids) oww of E 1070 polyacrylate followed by heat curing at 150°C for 15 minutes. The results appear below:

Example No	Metal Salt	Time to Exhaustion (min.)	Area Shrinkage (%)	
			1 hr	3 hr
23	$\text{MgCl}_2$	60	0	6
24	$\text{CaCl}_2$	80	0	14

#### Examples 25–27

The procedure of Example 8 was repeated using Hercosett 57 (Hercules) polyamide-epichlorohydrin resin together with an anionic exhaustion agent, sodium hexametaphosphate, commercially available as Calgon PT. Heat curing at 140°C for 15 minutes was used. The results appear below:

Example No.	% of Hercosett 57 oww	Time to Exhaustion (min.)	Area Shrinkage (%)	
			1 hr	3hr
25	10	45	1	6
26	8	25	2	7
27	6	30	5	11

#### Examples 28–33

In order to determine the effect of concentration of metal salt, Example 11 was repeated using different concentrations of  $\text{MgCl}_2$ . In each case the fabric was dried and heat cured at 140°C for 15 minutes.



5	Example No.	MgCl <sub>2</sub> Conc.	Time to Exhaustion (min.)	Area Shrinkage (%)	
				1 hr	3 hr
	28	4	60	0	0
	29	5	40	0	0
	30	6	30	0	0
10	31	7	20	1	3.4
	32	8	15	1.4	5.5
	33	10	12	0.4	6.4

5

10

15 It can be seen that the rate of exhaustion is controlled by the concentration of MgCl<sub>2</sub>. Rapid exhaustion times are generally not preferred since the washability and handle of the treated goods may not be up to the standard obtainable with more controlled exhaustion.

15

#### Examples 34-38

20 Examples 28 to 33 were repeated using 7 g/l MgCl<sub>2</sub> and varying the temperature of the bath. Heat curing was employed as before. The results of wash tests are given below.

20

25	Example No.	Bath Temperature	Time to Exhaustion (min.)	Area Shrinkage (%)	
				1 hr	3 hr
	34	30°	50	0	5
30	35	40°	35	0	5.3
	36	50°	20	0.5	3.5
	37	60°	16	1	2.5
	38	70°	12	1	6.4

25

30

#### Examples 39-43

40 Examples 28 to 33 were repeated using different ratios of BAP/Impranil DLH applied across the range. 2.0% BAP/0% DLH to 0% BAP/2% DLH with 2% total solids applied. Exhaustion time was maintained constant (at 45 min.) by varying the MgCl<sub>2</sub> concentration according to ratio of polymers. Curing was by dry heat at 140°C for 15 minutes. The results of wash tests were as follows:

35

40

45	Example No.	% BAP oww	% DLH oww	MgCl <sub>2</sub> conc. g/l	Area Shrinkage (%)	
					1 hr.	3 hr
	39	2.0	0	9.0	0	1
	40	1.5	0.5	7.0	1.5	0.5
	41	1.0	1.0	6.0	1	1
50	42	0.5	1.5	3.0	0.5	1
	43	0	2.0	3.5	9.8	30.3

45

50

#### Examples 44-47

55 Examples 28 to 33 were repeated on knitted fabric. The fabric used was single jersey wool fabric knitted from 2/24's worsted yarn to a cover factor of 1.1. It was scour d with 1 g/l non-ionic detergent (Lissapol N) and 2 g/l Na<sub>2</sub>SO<sub>4</sub> at 40°C for 10 minutes, followed by rinsing.

55

60 Samples of fabric were run in a bath containing 1.5% BAP, 1.5% DLH oww and between 4 and 10 g/l MgCl<sub>2</sub>. The temperature was set at 50°C, pH 7 and maintained until exhaustion was complete. Fabric samples were then heat cured at 140°C for 15 minutes.

60

5	Example No.	MgCl <sub>2</sub> conc. g/l	Time to Exhaustion (min.)	Area Shrinkage (%)		5
				1 hr wash	3 hr wash	
	44	4	44	1	4	
	45	6	22	0	6	
10	46	8	11	1	3	10
	47	10	7.5	0	5	
	Untreated fabric				70	

15 *Examples 48-50* 15

Example 45 was repeated using 2% BAP (solids oww) and 1% DLH (solids oww) at pH 7, 50°C, maintained until exhaustion complete. Samples were then either:

- 20 (a) removed from the bath at pH 7 and tumble dried, 20  
 (b) cured in the bath by raising the pH to 8 and holding for 10 minutes followed by tumble drying, or  
 (c) cured in the bath by raising the pH to 9 and holding for 10 minutes followed by tumble drying.

25 25

Example No.	Curing conditions	Area Shrinkage (%)		30
		1 hr	3hr	
30 48	Removed at pH 7	1	15	30
49	Bath to pH 8 for 10 min.	1	1	
50	Bath to pH 9 for 10 min.	1	1	

35 *Examples 51-53* 35

Samples of fabric cured as in Examples 48 to 50 were then dyed with a chrome dye, Eriochrome Black PV 200%, without drying. The dyebath contained:

4% Eriochrome Black PV 200%  
 3% Acetic acid (oww)

- 40 Dye and acid were added to the bath at 30°C and the fabric run for 10 minutes. The 40  
 temperature was then raised to the boil over 45 minutes and held for 30 minutes. 1.5% formic acid was then added and boiling continued for a further 30 minutes when the bath was cooled to 80° and 1.5% potassium dichromate added. The bath was returned to the boil and held for 45 minutes, followed by cold rinsing and tumble drying. An untreated control was included in  
 45 the dyebath. Wash results were:- 45

Example No.	Curing Conditions	Area Shrinkage during dyeing	Area Shrinkage (%)		50
			1 hr	3 hr	
51	Bath to pH 9 × 10 min.	0	3.0	14.0	
52	Bath to pH 8 × 10 min.	0	8.6	12	
53	Removed at pH 7	6.0	70%	—	
55 —	Untreated wool	7.4	72%	—	55

*Examples 54-56*

- 60 Example 45 was repeated on a Shetland fabric. The fabric was knitted to a cover factor of 0.9 60  
 from 2/8's Shetland yarn. The fabric was scour d with 1 g/l non-ionic detergent (Lissapol N) and 2 g/l Na<sub>2</sub>SO<sub>4</sub> at 40°C for 10 minutes, followed by rinsing.

65 Samples were heated in a bath of liquor ratio 40:1 set at pH 7 and 50°C containing 6 g/l 65  
 MgCl<sub>2</sub> and either 2.5%, 2.0% or 1.5% (solids) oww BAP/DLH at a ratio of 1:1. The temperature and pH were maintained until exhaustion was complete. Fabrics were then heat cured at 140°C for 15 minutes.

5	Example No.	% BAP/IMP oww	Time to Exhaustion (min.)	Area Shrinkage (%)		5
				1 hr wash	3 hr wash	
	54	2.5	45	0	0	
	55	2.0	40	1.8	2.3	
10	56	1.5	45	1.4	6.25	10
	Untreated fabric			35	61	

15 *Examples 57-59* 15

Example 54 was repeated using different curing conditions. Exhaustion was complete in 60 minutes. Fabrics were then cured as follows:

- (i) Removed at pH 7 and tumble dried at 100°C for 20 minutes.  
(ii) Bath pH raised to pH 8 and held for 15 minutes, tumble dried at 100°C for 20 minutes.  
20 (iii) Bath pH raised to pH 9 and held for 15 minutes, tumble dried at 100°C for 20 minutes. 20

25	Example No.	Curing conditions	Area Shrinkage (%)		25
			1 hr wash	3 hr wash	
	57	Removed at pH 7	4.5	10.5	
	58	Bath to pH 8 for 15 min.	0.8	2	
30	59	Bath to pH 9 for 15 min.	3	1.9	30

*Example 60*

500 g of a 4/8's hand knitting yarn were scoured in a laboratory hank dyeing machine at a liquor ratio of 30:1 containing 1 g/l nonionic detergent (Lissapol N) and 2 g/l Na<sub>2</sub>SO<sub>4</sub> at 40°C for 10 minutes, followed by rinsing. The bath was then set at a liquor ratio of 30:1 at pH 9, 35 50°C, containing 3.0% (solids) oww BAP/IMPANIL DLH at a ratio of 1:1 and 4 g/l MgCl<sub>2</sub>. 35 The pH and temperature were maintained until exhaustion was complete. The yarn was then rinsed and dried at 140°C for 15 minutes. Samples of fabric were then knitted to a cover factor of 0.9 and wash tested in the Cubex machine with the following results:

45		Area Shrinkage (%)		45
		1 hr	3 hr	
	Treated 3% BAP/DLH	6.5	12	
	Untreated	58	—	

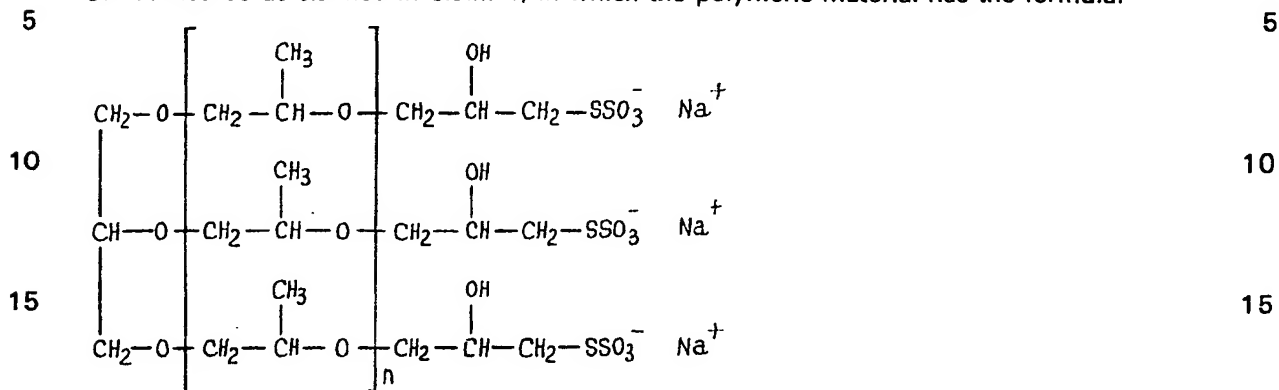
50 CLAIMS 50

1. A method of treating textiles which comprises applying to the textile a water-soluble curable polymeric material in an aqueous medium, simultaneously or subsequently applying to the textile a compatible exhaustion agent which reduces the solubility of the polymeric material, allowing the polymeric material to exhaust onto the textile and curing the polymeric material.  
55 2. A method as claimed in Claim 1, in which the polymeric material is a polymer having 55 ionic charges.  
3. A method as claimed in Claim 2, in which the polymeric material is a Bunte salt compound or a poly(carbamoylsulphonat).  
4. A method as claimed in Claim 2, in which the curable polymeric material has a polymeric 60 chain backbone and at least two thiosulphate groups per molecule. 60  
5. A method as claimed in Claim 2, in which the polymeric material has been prepared from a polymeric di- or poly-isocyanate by reaction with a bisulphite.  
6. A method as claimed in Claim 4, in which the polymeric material comprises a polymeric chain backbone and at least two isocyanate groups per molecule.  
65 7. A method as claimed in Claim 4 or 6, in which the polymeric backbone chain is a 65

polyoxyalkylene chain.

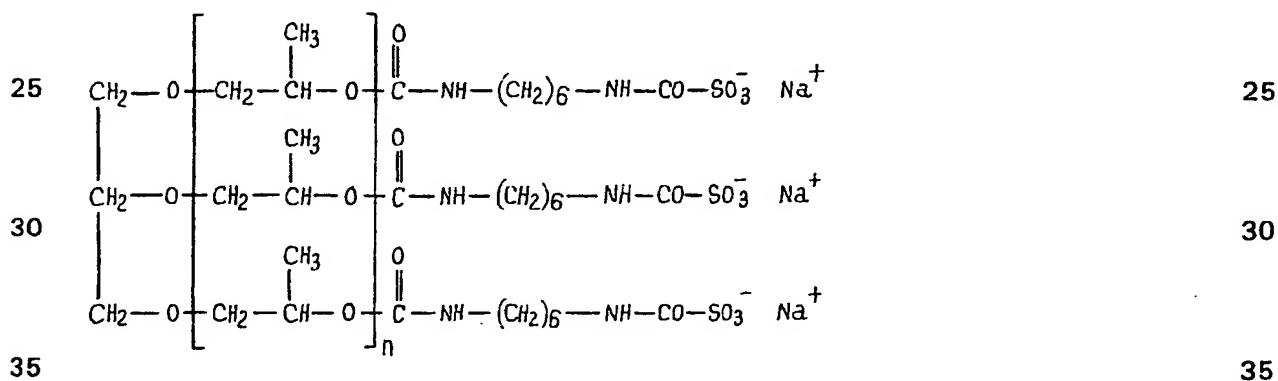
8. A method as claimed in Claim 7, in which the polyoxyalkylene chain is a polyoxypropylene chain.

9. A method as claimed in Claim 4, in which the polymeric material has the formula:



20 where n is about 13.

10. A method as claimed in Claim 5, in which the polymeric material has the formula:



where n is about 13.

11. A method as claimed in any of claims 1 to 10, in which the amount of polymeric material applied is between  $\frac{1}{2}$  and 10% on the weight of fibres.

40 12. A method as claimed in Claim 11, in which the amount of polymeric material applied is in the range of 2 to 4% on the weight of the fibres.

13. A method as claimed in any one of claims 1 to 12, in which the polymeric material is cured by means of an alkali.

45 14. A method as claimed in Claim 13, in which alkali is present in the aqueous medium containing the polymer from the start of the process.

15. A method as claimed in Claims 1 to 4, in which the alkali is pre-mixed with the polymeric material for an ageing period before application to the textile.

16. A method as claimed in Claim 15, in which the ageing period is from 10 to 60 minutes.

50 17. A method as claimed in Claim 13, in which the alkali is applied after exhaustion of the polymer from the aqueous medium.

18. A method as claimed in any one of claims 13 to 17, in which the alkali is ammonium hydroxide or trisodium phosphate.

19. A method as claimed in any one of Claims 13 to 18, in which sufficient alkali is used to ensure a pH value of 8 to 10.

55 20. A method as claimed in any one of claims 1 to 9, in which the exhaustion agent is neutral inorganic salt.

21. A method as claimed in Claim 20, in which the inorganic salt is selected from alkali metal, alkaline earth metal and ammonium salts of strong acids.

60 22. A method as claimed in Claim 21, in which the exhaustion agent is selected from sodium sulphate, sodium iodide, sodium chloride, magnesium sulphate, ammonium sulphate, calcium chloride and zinc sulphate.

23. A method as claimed in Claim 21, in which the exhaustion agent is magnesium chloride.

65 24. A method as claimed in any one of claims 1 to 23, in which the amount of exhaustion agent used is between 1 and 100 g/l of the treatment liquor.

25. A method as claimed in Claim 24, in which the amount of exhaustion agent is between 5 and 10 g/l of the treatment liquor.
26. A method of treating textiles as claimed in Claim 1, using a short liquor, in which;
- 5 (i) the polymeric material and alkali are mixed and allowed to age; 5  
(ii) the liquor from (i) is applied to the goods in a washing machine or milling machine;  
(iii) the goods are agitated until a uniform distribution of the liquor is obtained;  
(iv) a solution of inorganic salt is sprayed onto the goods and agitation continued until it is evenly distributed; and  
(v) the goods are rinsed, hydroextracted and dried.
- 10 27. A method of treating textiles as claimed in Claim 1, using a long liquor in which; 10  
(i) the polymer and alkali are mixed and added to the bath containing the goods;  
(ii) the solution of the inorganic salt is added and the temperature raised to 50°C;  
(iii) after about 30 minutes a further addition of inorganic salt is added; and  
(iv) after a further 15 to 30 minutes the goods are hydroextracted and dried.
- 15 28. A method as claimed in any one of Claims 1 to 27, wherein the textile material is a 15  
keratinous material.
29. A method as claimed in Claim 28, wherein the textile material is wool.
30. A method as claimed in Claim 28 or 29, wherein the textile material is in the form of knitted piece goods or garments.
- 20 31. A method as claimed in Claim 1, conducted and substantially as described in any of 20  
Examples 1 to 60, herein.
32. Textiles wherein treated by a method as claimed in any of Claims 1 to 31.

